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COPPER CMP SLURRY COMPOSITION

FIELD AND BACKGROUND OF THE INVENTION

5 The present invention relates to the field of metallurgy and specifically to a method for chemical-mechanical planarization (CMP) of copper-containing surfaces as well as a slurry composition useful for CMP.

10 In the manufacture of integrated circuits it is common to connect the various components with a network of thin planar wiring (also called interconnects) so as to reduce circuit volume and thus increase component density, for example, as is necessary in submicron multilevel microelectronics. Copper, due to its low resistivity and high electromigration resistance, is one of the best materials from which to manufacture planar interconnects.

15 The copper damascene process is the preferred method for the production of copper interconnects. In the copper damascene process the required pattern of interconnects is made on a dielectric substrate such as a silicon wafer, copper is deposited onto the pattern (e.g. by electroplating deposition) and thereafter planarized. Due to the fact that copper is a soft metal without a protective native oxide, mechanical planarization techniques give poor results, often resulting in uneven surfaces, generating internal stress or even cracking the interconnects.

20 Compared to purely mechanical planarization, significantly better results are obtained by planarization of copper interconnects using chemical-mechanical polishing (CMP). CMP is substantially abrasion of a copper surface in the presence of an oxidizing composition and fine particulate abrasives, together making a slurry. In CMP, a copper surface to be polished is held against a mechanical polishing device
25 (often a rotating polishing wheel) while being immersed in the slurry. By a combination of mechanical abrasion and chemical oxidation, thin layers of copper are removed. A detailed background of CMP can be found in, for example, U.S. Patent 4,671,851; U.S. Patent 4,910,155; U.S. Patent 4,944,836; U.S. Patent 5,676,587, U.S. Patent 5,840,629 and U.S. Patent 6,126,853.

30 Conceptually, CMP can be considered a two-step process.

In a first step, a layer of bare copper metal is oxidized by oxidizing agents in the slurry. In a second step, the oxidized layer is removed by the mechanical action of

the fine abrasive particles in the slurry, leading to a net removal of copper. An advantage of CMP is that since only an oxide layer is abraded, no mechanical stress is applied to the bulk of the copper. Further, areas that are not to be abraded are coated with a protective oxide layer.

5 An ideal CMP process is a process whereby copper metal is removed only through conversion to oxide and subsequent abrasion. As a result, the efficiency and efficacy of a CMP process are in a large part determined by the reactivity of the slurry. An ideal slurry is preferably fast-acting, quickly oxidizing newly exposed copper both to protect the surface and to generate a new oxide layer to be removed.

10 Ideally, copper is removed only by formation of an oxide, which in turn is removed only by abrasion. When either oxide or metal are soluble in the slurry, pitting and uneven planarization result. Therefore, a copper CMP slurry is preferably configured so that neither copper metal nor a produced copper oxide is soluble therein.

15 It is known that copper is soluble in acidic solutions. Despite this, acidic slurries are often used in CMP of copper based on the belief that the slurry passivates the copper, that is, oxidation occurs so quickly that dissolution of copper metal is not significant. Such slurries give less than ideal results.

20 It has been proposed to inhibit copper dissolution in acidic solutions by non-native passivation, that is the addition of reagents such as benzotriazole, that form a passivating film on exposed copper metal, see for example, U.S. Patent 6,569,350 and U.S. Patent 5,770,095. The rate of formation of such non-native passivation films has been found to be too slow to be effective during the rapid surface abrasion conditions of CMP.

25 A number of methods using non-acidic slurries have been proposed for the CMP of copper.

 Neutral or mildly basic slurries having a pH of up to about 9 have been disclosed, including U.S. patent 5,770,095, U.S. patent 5,800,577 and U.S. patent 5,840,629.

30 U.S. Patent 6,126,853, U.S. Patent 6,309,560 and U.S. Patent 6,569,350 teach compositions having a preferred pH of up to 8 and including a film-forming agent. U.S. Patent 6,432,828 teaches a related composition having a preferred pH of up to 8

but devoid of a film-forming agent. Mentioned in passing in all these patents is that the pH of the slurries can be raised up to 9 or even 12, but such high pH ranges are not actually taught. Further, in these slurries the use of metal ions in the slurry composition is expressly forbidden.

5 A few compositions more basic than pH 9 have also been discussed in the art. An ammonium hydroxide containing slurry with a pH of between 11 and 12 has been proposed (Streigerwald *et al.*, J. Electrochem. Soc. 142 (1995) p.2379). A slurry for the CMP of copper having a pH greater than or equal to 7, a copper oxidizing agent and ammonia as a copper complexing agent is taught in U.S. Patent 6,676,484. In
10 these slurries, copper is oxidized to form soluble ammonium salts (*e.g.* $\text{Cu}(\text{NH}_3)_2$) which are then dissolved by the slurry, in a manner analogous to the removal of copper metal by acidic slurries with the same disadvantages.

 It would be highly advantageous to have a slurry composition suitable for use in chemical-mechanical planarization of copper and copper alloys not having the
15 disadvantages of prior art.

SUMMARY OF THE INVENTION

 The above and other objectives are achieved by the teachings of the present invention.

20 The teachings of the present invention provide a composition useful for the formation of a passivating layer on a copper-containing surface. The teachings of the present invention also provide a method for making the composition and uses of the composition. As used herein, a passivating layer is a layer of copper oxides that is substantially insoluble in the composition itself. As used herein a copper-containing
25 surface is a surface of a metal or a metal alloy that contains more than about 5%, more than 10%, more than 20%, more than 40%, more than 50% or more than 80% copper by weight.

 As is clear to one skilled in the art, a composition of the present invention is useful, for example, as a slurry in the CMP of a copper-containing surface.

30 According to the teachings of the present invention there is provided a composition useful for the formation of a passivating layer on a copper-containing surface, the solution having a pH equal to or greater than about 9 and having an

oxidation potential sufficient to oxidize the surface to form copper oxides, wherein neither copper nor the formed copper oxides are substantially soluble in the composition. Preferably, the pH of the solution is no greater than about 13.

According to the teachings of the present invention there is also provided for
5 the use of a composition of the present invention for forming a passivating layer on a copper-containing surface.

According to the teachings of the present invention there is also provided a method of forming a passivating layer on a copper-containing surface, by contacting the surface with a composition of the present invention.

10 According to the teachings of the present invention there is also provided a method for planarizing a copper-containing surface, by abrading the surface in the presence of a composition of the present invention.

According to a feature of the present invention, a sufficient oxidation potential is an oxidation potential that is more positive than about P_{pH} volt relative to a
15 saturated calomel reference electrode, where:

$$P_{pH} = -0.05 \times pH + 0.425$$

And where pH is the pH of the composition.

20 In one embodiment of the present invention, when the pH of a solution is between 9 and 10, a sufficient oxidation potential is an oxidation potential that is more positive than about -0.05 volt relative to a saturated calomel reference electrode.

In another embodiment of the present invention, when the pH of a solution is between 10 and 11, a sufficient oxidation potential is an oxidation potential that is
25 more positive than about -0.1 volt relative to a saturated calomel reference electrode.

In another embodiment of the present invention, when the pH of a solution is between 11 and 12, a sufficient oxidation potential is an oxidation potential that is more positive than about -0.15 volt relative to a saturated calomel reference electrode.

In another embodiment of the present invention, when the pH of a solution is
30 between 12 and 13, a sufficient oxidation potential is an oxidation potential that is more positive than about -0.2 volt relative to a saturated calomel reference electrode.

In other embodiments of the present invention, a sufficient oxidation potential is an oxidation potential that is more positive than about -0.2V, -0.15V, -0.10V, -0.05V, 0.0V, 0.05V, 0.10V, 0.15V, 0.20V, 0.25V, 0.3V, 0.35V, 0.40V, 0.45V, 0.50V, 0.55V, 0.60V, 0.65V or 0.7V relative to a saturated calomel reference electrode. In an embodiment of the present invention, the oxidation potential is more positive than a saturated calomel reference electrode by an oxidation potential of at least 0.0V due to a general improvement in the structure and other properties of the oxide layer.

In a particular embodiment of the present invention, a composition includes a) a cation selected from the group of alkaline metal cations and alkaline earth metal cations and b) an anion of a weak acid.

Cations suitable in formulating a composition of the present invention include
 5 Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} .

Anions suitable in formulating a composition of the present invention include anions of weak acids, such as acids having a pK_a of greater than about 0. Suitable anions include, but are not limited to anions chosen from the amongst acetate, adipate, bicarbonate, bisulfate, carbonate, chloroacetate, citrate, crotonate, cyanate, glutarate,
 10 dihydrogen phosphate, hydrogen phosphate, hydrogen sulfate, hydroxide, d-lactate, l-lactate, d-malate, l-malate, maleate, d-mandelate, l-mandelate, malonate, oxalate, permanganate, phosphate, hydrogen phthalate, phthalate, propanoate, succinate, sulfanilate, sulfate, d-tartarate and l-tartarate.

In a preferred embodiment of the present invention, the cation is K^+ and the
 15 anion is carbonate. In another preferred embodiment of the present invention, the cation is Cs^+ and the anion is carbonate.

According to a feature of the present invention, a composition of the present invention also includes an oxidizing agent. Suitable oxidizing agents include but are not limited to phenols, peroxides, permanganates, chromates, iodates, iron salts,
 20 aluminum salts, sodium salts, potassium salts, phosphonium salts, chlorates, perchlorates, persulfates and mixtures thereof. Examples of suitable oxidizing agents include phenol, KIO_3 , KBrO_3 , $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{K}_2\text{Cr}_2\text{O}_7$, V_2O_3 , H_2O_2 , HOCl , KOCl and KMgO_4 and in particular KMnO_4 .

The teachings of the present invention provide a method for passivating a
 25 copper surface by the formation of oxides so there is no need for non-native

passivation. Therefore, according to a feature of the present invention, a composition of the present invention is substantially devoid of a film-forming agent as defined in U.S. Patent 5,770,095 and U.S. Patent 6,569,350 and including cyclic compounds such as azole, triazole, imidazole, benzotriazole, benzimidazole and benzothiazole and their derivatives with hydroxy, amino, imino, carboxy, mercapto, nitro and alkyl substituted groups as well as urea and thiourea, salicylaldehyde, cupferron, ethylenediamine, amino acids containing sulfur, p-aminobenzaldehyde, halo acetic acids, thiols such as phosphonic acids (*e.g.*, dodecylmercaptan and octanephosphonic acid), monosaccharides and N-benzoyl-N-phenylhydroxyamine.

According to a feature of the present invention, a composition of the present invention is substantially devoid of copper complexing agents such as ammonium cations so as to avoid dissolution of copper metal by the composition.

According to a feature of the present invention, a composition of the present invention includes abrasive particles, such as metal oxides. Suitable metal oxides include but are not limited to oxides of aluminum, cerium, germanium, silicon, titanium, zirconium and mixtures thereof. Specific examples of suitable abrasives include SiO_2 , CeO_2 , Al_2O_3 , SiC , Si_3N_4 and Fe_2O_3 . In one embodiment of the present invention the abrasive particles make up between about 1% and 30% by weight of the composition.

According to the teachings of the present invention there is also provided a method for preparation of a composition of the present invention by preparing a solution having a pH equal to or greater than about 9 and having an oxidation potential sufficient to oxidize the surface to form copper oxides, wherein neither copper nor the formed copper oxides are substantially soluble in the composition.

According to a feature of the method of the present invention, a composition is prepared by providing a solution including water and adding to the solution a cation selected from the group consisting of alkaline metal cations and alkaline earth metal cations and an anion of a weak acid in an amount so that the pH of the solution is equal to or greater than about 9 and also adding to the solution an oxidizing agent so that the oxidation potential of the solution is more positive than about P_{pH} volt relative to a saturated calomel reference electrode, where:

$$P_{\text{pH}} = -0.05 \times \text{pH} + 0.425$$

and where pH is the pH of the solution.

Suitable oxidizing agents added include but are not limited to phenols, peroxides, permanganates, chromates, iodates, iron salts, aluminum salts, sodium salts, potassium salts, phosphonium salts, chlorates, perchlorates, persulfates and mixtures thereof, examples including phenol, KIO_3 , KBrO_3 , $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{K}_2\text{Cr}_2\text{O}_7$, V_2O_5 , H_2O_2 , HOCl , KOCl and KMgO_4 and in particular KMnO_4 .

According to a feature of the method of the present invention, a composition of the present invention is prepared by adding abrasive particles, such as metal oxides, to the solution. Suitable metal oxides include but are not limited to oxides of aluminum, cerium, germanium, silicon, titanium, zirconium and mixtures thereof. Specific examples of suitable abrasives include SiO_2 , CeO_2 , Al_2O_3 , SiC , Si_3N_4 and Fe_2O_3 . In one embodiment of the present invention the abrasive particles are added so as to make up between about 1% and 30% by weight of the composition.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described below. In case of conflict, the patent specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention is herein described, by way of example only, with reference to the accompanying drawings. With specific reference now to the drawings in detail, it is stressed that the particulars shown are by way of example and for purposes of illustrative discussion of the preferred embodiments of the present invention only, and are presented in the cause of providing what is believed to be the most useful and readily understood description of the principles and conceptual aspects of the invention. In this regard, no attempt is made to show structural details of the invention in more detail than is necessary for a fundamental understanding of the invention, the

description taken with the drawings making apparent to those skilled in the art how the several forms of the invention may be embodied in practice.

In the drawings:

FIG. 1 is the Pourbaix diagram of copper (Potential-pH equilibrium diagram of copper-water system at 25°C considering the solid substances Cu, Cu₂O, and CuO) [Cu²⁺]=10⁻⁶ M) from "Atlas of Equilibrium in Aqueous Solutions", M. Pourbaix, NACE, Houston Texas, USA (1975);

FIG. 2A depicts corrosion potential transients of copper at 25°C in not deaerated sodium hydroxide solutions;

FIG. 2B depicts corrosion potential transients of copper at 25°C in deaerated sodium hydroxide solutions;

FIG. 3A depicts anodic polarization curves of copper at 25°C in not deaerated sodium hydroxide solutions at a scan rate of 5mV/s;

FIG. 3B depicts anodic polarization curves of copper at 25°C in deaerated sodium hydroxide solutions at a scan rate of 5mV/s;

FIGS. 4A-4C depict anodic polarization curves of copper measured at various scan rates subsequent to cathodic pretreatment at -1.5V for 5 minutes in 0.3 g/l (Fig. 4A), 3 g/l (Fig. 4B) and 30 g/l (Fig. 4C) sodium hydroxide solutions;

FIG. 5 depicts current transients of copper measured with potentiostatic exposure of copper electrodes at various applied potentials in a 3g/l sodium hydroxide solution;

FIGS. 6A-6G are high-resolution scanning electron microscope images of various copper surfaces after 30 minutes exposure at different applied potentials in 3g/l sodium hydroxides including a polished copper surface (Fig. 6A), -0.4V (Fig. 6B and 6C), -0.15V (Fig. 6D and 6E) and 0.3V (Fig. 6F and 6G);

FIGS. 7A-7G are high-resolution scanning electron microscope images of various copper surfaces after various exposure times to OCP in 3g/l sodium hydroxides 30minutes (Fig. 7A), 60 minutes (Fig. 7B and 7C), 160 minutes (Fig. 7D and 7E) and 300 minutes (Fig. 7F and 7G);

FIG. 8 depicts the corrosion potential transients of copper in a 3 g/l sodium hydroxide solution subsequent to 10 minute exposure to -0.15V followed by 30 minutes exposure to more positive potentials;

FIG. 9 depicts the corrosion potential transient of copper in a 3 g/l sodium hydroxide after different potentiostatic pretreatments;

FIGS. 10A-10C are high-resolution scanning electron microscope images of various copper surfaces developed in 3 g/l sodium hydroxide solutions at -0.15V for 10 minutes (Fig. 10A), 0.7V for 15 minutes (Fig. 10B) and initially pre-treated at -0.15V for 10 minutes followed by 0.7V potential for 60 seconds (Fig. 10C);

FIG. 11 is a potentiodynamic profile of copper in a K_2CO_3 solution with and without the addition of KMnO_4 as an oxidizing agent; and

FIG. 12 is a graph of the cyclic polarization of copper in a K_2CO_3 solution containing KMnO_4 as an oxidizing agent.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is of a composition, a process for making the composition and uses for the composition. A composition of the present invention is useful for the formation of a passivating layer on a copper-containing surface. By passivating layer is meant a layer of copper oxides that is substantially insoluble in the composition itself. As is clear to one skilled in the art, a composition such as a composition of the present invention that forms a passivating oxide layer is useful, for example, as a slurry in the CMP of a copper-containing surface.

The present invention also provide for the use of a composition of the present invention for forming a passivating layer on a copper-containing surface.

The present invention also provides a method of forming a passivating layer on a copper-containing surface, by contacting the surface with a composition of the present invention.

The present invention also provides a method for planarizing a copper-containing surface, by abrading the surface in the presence of a composition of the present invention.

As used herein, the term "process" and the term "method" refers to manners, means, techniques and procedures for accomplishing a given task including, but not limited to, those manners, means, techniques and procedures either known to, or readily developed from known manners, means, techniques and procedures by

practitioners of the chemical, pharmacological, biological, biochemical and medical arts.

The principles and uses of the processes, compositions and methods of the present invention may be better understood with reference to the description and examples hereinbelow.

Before explaining at least one embodiment of the invention in detail, it is to be understood that the invention is not limited in its application to the details set forth in the following description or exemplified by the Examples. The invention is capable of other embodiments or of being practiced or carried out in various ways. Also, it is to be understood that the phraseology and terminology employed herein is for the purpose of description and should not be regarded as limiting.

The present invention is based on using a basic solution having a pH equal to or greater than about 9 that passivates a copper-containing surface, that is the surface is rapidly oxidized to yield a uniform layer of substantially insoluble copper oxides, apparently CuO or Cu_2O . It has been unexpectedly found that a solution having a pH of equal to or greater than about 9 and wherein copper is substantially insoluble can passivate a copper-containing surface by forming a layer of copper oxides that are substantially insoluble in the composition, if the oxidation potential of the solution is sufficient.

The teachings of the present invention define the parameters of a composition that is fast-acting, quickly oxidizing bare copper to form an oxide layer. At the same time, the composition is formulated so that neither copper metal nor oxides formed are significantly soluble in the slurry. Certain compositions of the present invention form thin oxide layers composed of homogeneously sized oxide particles, oxide layers that are known in the art as being useful for CMP.

While not wishing to be held to any one theory, it is believed that the unexpected efficacy of an oxidizing solution having a pH of greater than about 9 as a copper passivating solution can be explained by understanding the chemistry of copper oxidation with the help of the Pourbaix diagram (Figure 1) describing the electrochemical properties of copper.

From the Pourbaix diagram it is seen, from the line labeled 7, that copper can be passivated in slurries having a pH between about 7 and about 13. From the

Pourbaix diagram it is also seen that at pHs above 13 copper is dissolved by the formation of soluble cuprite ions (CuO_2^-). From the Pourbaix diagram it is seen that depending on the pH of a composition, a sufficient oxidation potential for passivation is more positive than -0.2V, -0.15, -0.10, -0.05, 0.0, 0.05, 0.1, 0.15, 0.20, 0.25, 0.3, 0.35, 0.40, 0.45, 0.50, 0.55, 0.60, 0.65 and up to about 0.7V.

The minimal value of a "sufficient oxidation potential" for a given solution depends on the pH of the solution. From the Pourbaix diagram it is seen that for a solution with a pH of between about 9 and about 10, a sufficient oxidation potential is more positive than about -0.05 volt relative to a saturated calomel reference electrode, for a solution with a pH of between about 10 and about 11, a sufficient oxidation potential is more positive than about -0.1 volt relative to a saturated calomel reference electrode, for a solution with a pH of between about 11 and about 12, a sufficient oxidation potential is more positive than about -0.15 volt relative to a saturated calomel reference electrode and that for a solution with a pH of between about 12 and about 13, a sufficient oxidation potential is more positive than about -0.2 volt relative to a saturated calomel reference electrode.

From Figure 1 it is seen that the equation of the line labeled 7 is roughly

$$P_{\text{pH}} = -0.05 \times \text{pH} + 0.425$$

20

where pH is the pH of a solution and P_{pH} is the potential, in units of volts relative to a saturated calomel reference electrode, above which the oxidation potential of a solution must be to be sufficient for passivation of a copper-containing surface as defined herein.

25

It is important to remember that the Pourbaix diagram takes into account only the thermodynamics of oxidation (relative to a standard hydrogen electrode) and does not account for kinetic effects. The Pourbaix diagram can therefore be considered as doing no more than assisting one skilled in the art to understand the theoretical underpinnings of the present invention. The experimental results presented hereinbelow are necessary to reduce the invention to practice.

30

A preferred composition of the present invention is a solution including a) a cation selected from the group of alkaline metal cations and alkaline earth metal

cations; and b) an anion of a weak acid, and having a pH of greater than about 9. In such a solution, the basic environment necessary for effective copper passivation according to the teachings of the present invention is achieved.

Cations suitable for formulating a composition of the present invention include
5 Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} .

Anions suitable anions for formulating a composition of the present invention include anions of weak acids, such as acids having a pK_a of greater than about 0. Suitable anions include, but are not limited to anions chosen from the amongst acetate, adipate, bicarbonate, bisulfate, carbonate, chloroacetate, citrate, crotonate,
10 cyanate, glutarate, dihydrogen phosphate, hydrogen phosphate, hydrogen sulfate, hydroxide, d-lactate, l-lactate, d-malate, l-malate, maleate, d-mandelate, l-mandelate, malonate, oxalate, permanganate, phosphate, hydrogen phthalate, phthalate, propanoate, succinate, sulfanilate, sulfate, d-tartarate and l-tartarate.

In a preferred embodiment of the present invention, the cation is K^+ and the
15 anion is carbonate. In another preferred embodiment of the present invention, the cation is Cs^+ and the anion is carbonate.

In some cases, a composition of the present invention includes an oxidizing agent. Such cases include when a "sufficient oxidation potential" is not achieved only by the combination of the cation and anion described hereinabove or there is some
20 other reason such as a desire to change the kinetics of oxide formation, or a desire to change the exact nature of the oxide layer formed.

Suitable oxidizing agents added include both organic compounds (such as phenols) and inorganic compounds (such as peroxides, permanganates, chromates, iodates, iron salts, aluminum salts, sodium salts, potassium salts, phosphonium salts,
25 chlorates, perchlorates, persulfates and mixtures thereof). Examples of suitable oxidizing agents include phenol, KIO_3 , KBrO_3 , $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{K}_2\text{Cr}_2\text{O}_7$, V_2O_3 , H_2O_2 , HOCl , KOCl and KMgO_4 and in particular KMnO_4 .

One of the primary uses for a composition, such as the composition of the present invention, which is configured to passivate a copper-containing surface, is as a
30 CMP slurry. Therefore, in a preferred embodiment, a composition of the present invention includes abrasive particles, such as a metal oxide powder. Suitable metal oxides include but are no limited to oxides of aluminum, cerium, germanium, silicon,

titanium, zirconium and mixtures thereof. Specific examples of suitable abrasives include SiO_2 , CeO_2 , Al_2O_3 , SiC , Si_3N_4 and Fe_2O_3 . In one embodiment of the present invention the abrasive particles make up between about 1% and 30% by weight of the composition.

5 One of the many advantages of the teachings of the present invention is that a passivating composition can be formulated that is substantially devoid of a film-forming agent as defined in U.S. Patent 5,770,095 and U.S. Patent 6,569,350. Such film-forming agents are those listed in U.S. Patent 5,770,095 and U.S. Patent 6,569,350 and include cyclic compounds such as azole, triazole, imidazole,
10 benzotriazole, benzimidazole and benzothiazole and their derivatives with hydroxy, amino, imino, carboxy, mercapto, nitro and alkyl substituted groups as well as urea and thiourea, salicylaldehyde, cupferron, ethylenediamine, amino acids containing sulfur, p-aminobenzaldehyde, halo acetic acids, thiols such as phosphonic acids (*e.g.*, dodecylmercaptan and octanephosphonic acid), monosaccharides and N-benzoyl-N-
15 phenylhydroxyamine.

 One of the many advantages of the teachings of the present invention is that a passivating composition can be formulated that is substantially devoid of a copper-complexing agents such as ammonium cations. As is clear one skilled in the art and as mentioned in the introduction hereinabove, copper-complexing agents dissolve copper
20 metal, giving inferior CMP results.

 Preparation of a composition of the present invention involves preparing a solution having a pH equal to or greater than about 9 and having an oxidation potential sufficient to oxidize a copper-containing surface to form copper oxides, wherein neither copper nor the formed copper oxides are substantially soluble in the
25 composition.

 For example, a composition of the present invention is prepared by providing a solution including water and adding to the solution a cation selected from the group consisting of alkaline metal cations and alkaline earth metal cations and an anion of a weak acid in an aqueous solution in an amount so that the pH of the solution is equal
30 to or greater than about 9 and also adding to the solution an oxidizing agent so that the oxidation potential of the solution is sufficient, as defined hereinabove.

Suitable oxidizing agents to be added include but are not limited to phenols, peroxides, permanganates, chromates, iodates, iron salts, aluminum salts, sodium salts, potassium salts, phosphonium salts, chlorates, perchlorates, persulfates and mixtures thereof, examples including phenol, KIO_3 , KBrO_3 , $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{K}_2\text{Cr}_2\text{O}_7$,
 5 V_2O_3 , H_2O_2 , HOCl , KOCl and KMgO_4 and in particular KMnO_4 .

As discussed above, when preparing a composition of the present invention, especially a CMP slurry embodiment, abrasive particles, such as metal oxides, are preferably added to the solution, preferably so as to make up between about 1% and 30% by weight of the composition. Suitable metal oxides added include but are not
 10 limited to oxides of aluminum, cerium, germanium, silicon, titanium, zirconium and mixtures thereof. Specific examples of suitable abrasives include SiO_2 , CeO_2 , Al_2O_3 , SiC , Si_3N_4 and Fe_2O_3 .

Proof of Concept

To confirm and reduce the innovative hypothesis of the present invention to
 15 practice, the oxidation of copper in sodium hydroxide solutions was studied.

First, a 3 g/l sodium hydroxide solution having a pH of 12.5 (NaOH being the sodium salt of the weak acid water) was studied. According to the Pourbaix diagram (Figure 1), at pH 12.5 copper passivation is expected. The behavior of copper in sodium hydroxide solutions has been extensively investigated by many authors (*e.g.*:
 20 Feng *et al.* Corrosion 53 (1997) p. 389; Kunze *et al.* J. Phys. Chem. B 105 (2001) p. 4263; Strehblow *et al.* Electrochim. Acta 25 (1980) p. 839; Kautek *et al.* J. Electrochem. Soc. 133 (1986) p. 739; Hamilton *et al.* J. Electrochem. Soc. 139 (1992) p. 426; Chan *et al.* J. Phys. Chem B 103(1999) p. 357; Melendres *et al.* J. Electroanal. Chem. 449 (1998) p. 215; Maurice *et al.* J. Electrochem. Soc 146(2) (1999) p. 524)
 25 using many different analytical techniques, such as Raman spectroscopy, electrochemical measurements, scanning tunneling microscopy and X-rays photoelectron spectroscopy. The formation of different copper oxides including CuOH , Cu_2O , CuO has been observed in these investigations. It should be noted that the formation of CuOH was observed at the potential of $-0.675V_{\text{SHE}}$ (Maurice *et al.* J.
 30 Electrochem. Soc 146(2) (1999) p. 524). The formation of CuOH was confirmed by scanning tunneling microscopy (Maurice *et al.* Surface Science 458(2000) p.185), despite the fact that copper oxides formation at potentials below $-0.2V_{\text{SHE}}$ is not in

agreement with the Pourbaix diagram (Figure 1, this potential region is related to copper immunity in basic solutions). Herein were studied the features of copper oxides formation from -1.5V to 1V in sodium hydroxide solutions.

Understanding copper electrochemistry in hydroxide solutions – the effect of sodium hydroxide concentration

5 In order to understand the effect of pH on copper oxidation in basic solutions, also evaluated were solutions containing 0.3 and 30 g/l NaOH. The pHs of these two solutions were 10.5 and 14.0 respectively. The Pourbaix diagram (Figure 1) indicates that copper can be dissolved via the formation of soluble cuprite ions (CuO_2^-) at a pH above about 13. Thus, in a 30 g/l NaOH solution copper dissolution is expected in
10 addition to oxidation.

The corrosion potential transient of copper measured during open-circuit potential (OCP) exposure in sodium hydroxide solutions of 0.3, 3 and 30 g/l NaOH is shown in Figure 2A for a not-deaerated solution and in Figure 2B for a deaerated solution. In both the not-deaerated and deaerated solutions the value of the corrosion
15 potential decreased with an increase in the sodium hydroxide concentration. In the not-deaerated cell the corrosion potential sharply increased after immersion up to a certain value and thereafter remained substantially constant. The values of corrosion potentials obtained after one-hour exposure in a not-deaerated and deaerated cell are presented in Table I:

20

Table I: Copper corrosion potential values measured after one hour exposure in a not-deaerated and deaerated sodium hydroxide solutions.

	0.3 g/l	3 g/l	30 g/l
Not-deaerated cell	-0.15V	-0.21V	-0.31V
Deaerated cell	-0.375V	-0.515V	0.56V

The anodic potentiodynamic curves (scan rate of 5 mV/s) for copper after one-
25 hour exposure in the three alkaline solutions are shown in Figures 3.

In a not deaerated 30 g/l NaOH solution (Figure 3A) the onset of anodic current was detected at -0.32V and a broad current peak (A_2) was observed in the

anodic curve. With a decrease in NaOH concentration the onset of the anodic current shifted in the positive direction and the peak A_2 markedly decreased. In 0.3 g/l the A_2 peak practically disappeared.

5 In the deaerated solutions (Figure 3B) the onset of anodic current was observed at potentials below -0.5V and an additional anodic peak, A_3 , appeared at -0.5V. In the 3 g/l NaOH solution the anodic peak A_2 became smaller and shifted to more positive potential compared with 30 g/l NaOH solution.

10 In Figures 4 are presented the effects of cathodic pretreatment on the anodic behavior of copper electrodes. These results were obtained at various scan rates (between 5 and 1000 mV/s). Subsequent to the cathodic pretreatment (-1.5V for 5 minutes) the onset of anodic current was observed to be at potentials below -1.0V, in all the examined solutions. Additional anodic peaks (A_4 and A_5) were detected in the anodic profiles obtained for all the solutions at scan rates above 100 mV/s.

15 The peaks sequence from A_1 to A_5 is clearly observed in the 0.3 g/l NaOH solutions (Figure 4A) but were more pronounced in the 3 g/l NaOH solutions (Figure 4B) and even more pronounced in the 30 g/l NaOH solutions (Figure 4C). For example, the anodic peak A_2 in the polarization curve obtained at 5 mV/s of the 0.3 g/l NaOH is not well resolved but is well resolved in the polarization curves of the 3 g/l NaOH and 30 g/l NaOH solutions. The anodic currents obtained in all scan rates
20 increased with increase in NaOH concentration.

From these results it is seen that an increase in sodium hydroxide concentration causes a decrease in copper corrosion potential in both not-deaerated and deaerated solutions. In the more concentrated sodium hydroxide solutions the anodic current peak A_2 is more pronounced, that is the peak is broader and detected at
25 lower potentials. Similar copper electrochemical behavior was observed in polarization curves obtained subsequent to cathodic pre-treatment at -1.5V for 5 min, with various scan rates, at various sodium hydroxide concentrations.

Characteristics of copper oxides at the potential region above -0.25V

30 From the results above it is clear that copper oxidation in a sodium hydroxide solution strongly depends on the applied potential. For CMP applications, the most important feature is the nature of copper oxidation at E_{corr} and in the potential region

above E_{corr} . This potential region can be achieved with external polarization or by the addition of an oxidizing agent. The corrosion potential of copper can be shifted from OCP to a positive direction in a wide potential range by varying the nature and concentration of an oxidizing agent added to the solution. Such an addition by itself
5 can enhance passivation characteristics.

Further, the morphology of copper oxides and copper oxide transformation in potential region above -0.4V was studied. Special attention was given to potential region above OCP (-0.25V) in not deaerated solutions. As is clear to one skilled in the art, it is preferable to use not deaerated solutions for CMP as CMP becomes relatively
10 inexpensive once there is no need for deaeration equipment.

The morphology of copper oxides formed at different potentials (A_1 , A_2 and A_3 peaks) on rounded copper coupons (0.5 cm radius and 2 mm thick, 99.9995% purity) polished with a 1 μm diamond paste was studied. The oxide growth was conducted using potentiostatic exposure for 30 minute at the examined potentials (-
15 0.4V (A_3), -0.15V (A_2), and 0.3V (A_1)), applied after cathodic pre-treatment for 5 minutes at -1.5V. Subsequent to potentiostatic exposure, the coupons were rinsed with deionized water, dried and examined by high-resolution scanning electron microscopy.

The current transients measured during the exposure of the copper coupons at
20 different applied potentials are shown in Figure 5.

Following the application of -0.4V, the anodic current rapidly decreased down to a value lower than $1 \cdot 10^{-5} \text{ A/cm}^2$, indicating the formation of a copper oxide layer on the surface of the coupon.

In contrast, the behavior of the anodic current transient following the
25 application of -0.15V was observed to be completely different for the first 20 seconds. When the potential was applied, the anodic current rapidly decreased down to $1 \cdot 10^{-4} \text{ A/cm}^2$ as was observed for -0.4V. However, during further exposure (200 seconds) a peak in the profile of the anodic current transient with a maximum value of $8 \times 10^{-4} \text{ A/cm}^2$ was observed. After 600 seconds the anodic current decreased down to 1×10^{-5}
30 A/cm^2 . The anodic current peak observed during copper exposure at -0.15V is attributed to alteration in the nature of the copper oxide layer.

Following the application of 0.1V, the anodic current gradually decreased during exposure as was observed at -0.4V. However, unlike the situation observed at -0.4V the decrease in the anodic current at 0.1V was much slower, especially during the first 200 seconds. No peak of anodic current was detected during exposure at 0.1V. The detected peak was very small and observed after 10 seconds exposure. During further exposure the anodic current decreased to very low values (ca. 1×10^{-5} A/cm² after 200 seconds exposure).

The different anodic current transient profiles measured at different applied potentials are associated with variations in the nature of the produced oxide films.

The variations in the nature of the produced oxide films were examined using high-resolution scanning electron microscopy. Figures 6 show the surface morphology of a polished copper surface (Figure 6A) and copper surfaces exposed to different applied potentials corresponding to the anodic peaks A₁, A₂ and A₃ in 3 g/l sodium hydroxide solution.

Figures 6B and 6C show the oxides developed on copper after 30 minutes exposure at -0.4V. The copper oxide (apparently Cu₂O) covering the electrode surface after exposure at -0.4V is characterized as a dense layer with a deposition of small globular crystal having average dimensions of between 50 and 100 nanometer.

The morphology of the copper surface after exposure at -0.15V was completely different, Figures 6D and 6E. The whole surface was covered with a thick crystalline layer (probably CuO). This deposit had a two-layer structure: the lower layer consisting of small-elongated crystals (significantly lower than 1 micron) while the upper layer consisted of large needle-like crystals.

No deposits were observed after exposure to 0.3V (even at a x200000 magnification), Figures 6F and 6G. The appearance of the copper surface after exposure to 0.3V did not change and was similar to a freshly polished surface. Apparently, the copper oxide that formed at 0.3V was very thin and dense.

In order to determine the variations in copper oxides coating formed during copper exposure at OCP, the morphology of copper surfaces developed at different stages of OCP exposure was compared to the morphology obtained at different applied potentials. The results are shown in Figures 7.

Figure 7A was obtained after 30 minutes exposure at OCP in a 3 g/l NaOH solution. Only traces of copper oxide were detected on the copper surface.

The surface morphology obtained after 30 min exposure at OCP was very similar to the one detected at -0.4V, Figure 7B.

5 After a one-hour exposure, the copper surface was covered with deposits of both short (ca. 100 nm) and long (ca. 2 μ m) needle-like crystals (Figure 7C).

Changes observed upon further exposure were related only to crystal size.

After 2.5 hours the size of both short and long crystals increased up to 250 nm and ca. 6 microns respectively (Figures 7D and 7E).

10 After 5 hours exposure the short crystals reached ca. 500 nm length (Figures 7F and 7G). It is seen that the long crystals became distorted. It should be noted that the morphology of copper oxide crystals observed during OCP exposure differed from the morphology observed at -0.15V, compare to Figures 6D and 6E.

Based on these results it can be concluded that a copper surface exposed at 15 potentials below 0.0V is covered with flaky deposits of oxides. At potentials above 0.0V, a copper surface becomes covered with very thin, dense film of oxides.

Determination of copper passivation potential range needed for CMP

20 The transformation of copper oxides from one form to another was studied using the corrosion potential decay method. A copper electrode was first exposed to -0.15V for 10 minutes and thereafter to a more positive potential. In some cases the copper electrode was immediately exposed to potential above 0.0V. After interruption of potentiostatic exposure, the corrosion potential decay was measured. The results are shown in Figure 8 and Figure 9.

25 Figure 8 presents results of corrosion potential decay obtained after 10 minutes exposure to -0.15V followed with a shift in the applied potential to more positive values and further exposure for 30 min at the new applied potential. In Figure 8 it is seen that interruption of electrode exposure at -0.15V is accompanied by a rapid decrease in the corrosion potential down to values slightly below -0.2V. Similar 30 results were also obtained when exposure to -0.15V was followed by exposure to 0.2 and 0.3V. As is seen in Figure 8, a rapid drop to values below -0.2V accompanies interruption of polarization at 0.2 and 0.3V. The situation changes if pre-exposure at -

0.15V is followed by the potentiostatic exposure at 0.4V and higher potentials. As is seen in Figure 8, a marked potential delay occurred in the decay curves obtained after exposure to potentials higher than 0.3V. The higher the potential applied after exposure to -0.15V, the longer the potential delay in the decay curves. It is reasonable to assume that exposure at potentials 0.2 and 0.3V after pre-treatment at -0.15V is accompanied by the formation of very thin oxides on the electrode surface. At potentials above 0.3V either the thickness (or amount) of the new oxides increases or the transformation of oxides formed at -0.15V into different oxides occurs.

In order to determine the role of copper oxides covering electrode surface after exposure to -0.15V and the nature of copper oxides formed at potentials above 0.0V the potential decay after exposure at 0.7V with and without pretreatment at -0.15V was examined. The obtained results are shown in Figure 9. As is seen in Figure 9, once the potential of 0.7V is applied without pre-treatment at -0.15V the corrosion potential rapidly decreases without an intermediate delay. In contrast, exposure at 0.7V after pre-exposure at -0.15V results in a significant potential delay. The longer the exposure of the pre-treated electrodes at 0.7V, the wider the potential delay. It should be also noted that in all the cases when the delay occurred, the corrosion potential during long term exposure reached the potential values of approximately -0.15V.

These results provide evidence that the nature of copper oxides formed at potentials above 0.0V depends in a large part on the initial surface state of copper. It can be suggested that two different copper oxides are formed on the copper surface at potentials above 0.0V. In the case of bare copper, a thin oxide film is formed. If a copper oxide layer is formed on electrode surface during exposure at potentials below 0.0V, the transformation of the original copper oxide layer to a new type takes place when a potential of 0.7V is applied.

It is therefore seen that the potential region between 0.0V and 0.7V is characterized by the formation of two different copper oxides. The electrochemical measurements described hereinabove indicate that these oxides are different from the oxides formed at potentials below 0.0V. The copper oxides formed at potentials below 0.0V undergo transformation during increase of applied potentials above 0.0V.

The difference between copper oxide morphologies developed during potentiostatic exposure at -0.15V and 0.7V is clearly seen in Figures 10A and 10B. In Figure 10C, the transformation of copper oxide formed at -0.15V after an increase in the applied potential to 0.7V and further exposure for 30 minute is seen. As can be
5 seen, copper oxide formed on the untreated copper surface at 0.7V (Figure 10B) is dramatically different from the morphology observed at -0.15V (Figure 10A). Figure 10C presents the morphology developed at the copper surface exposed at 0.7V for 30 minutes after a pre-treatment process at -0.15V for 10 minutes. At -0.15V, the oxide has a two-layer structure: small crystals in a first layer and large crystals in an upper
10 layer. Comparing Figures 10A and 10C indicates that by applying a potential of 0.7V the first layer disappeared or changed to another form.

Conclusion

It can be concluded that copper oxides formed in solutions including an
15 alkaline metal cations or an alkaline earth metal cation and an anion of a weak acid, such as sodium hydroxide at potentials above 0.0V and in the pH range of between 7 and 12 are the most applicable for copper CMP application. These oxides are highly dense, thin and behave as a passive film. The combination of an aqueous solution with a pH of between 7 and 12, together with an oxidizing agent (instead of the external
20 power supply used herein) provide a passivation potential of up to 0.7V, although potentials of between 0.3V and 0.4V are sufficient.

These hypotheses were confirmed by the following examples.

EXAMPLES

25 Reference is now made to the following examples that, together with the above description, illustrate the invention in a non-limiting fashion.

EXAMPLE 1

Passivation of a copper surface using $KMnO_4$ / K_2CO_3 solutions

30 Three aqueous potassium carbonate solutions were prepared:

Solution I: 4 g/liter K_2CO_3 ;

Solution II: 4 g/liter K_2CO_3 with 0.01 g/liter $KMnO_4$; and

Solution III: 4 g/liter K_2CO_3 with 1 g/liter $KMnO_4$.

The pH of the three solutions was determined to be 12. The potentiodynamic profile of a copper plate was measured in solutions I, II and III. The results are depicted in Figure 11. From Figure 11 it is seen that copper is passivated in solution I only in the range of potentials between 0.0 and 550 mV. The addition of $KMnO_4$ in solutions II and III increases the passivation potential to 180 mV and 220 mV respectively.

Passivation of a copper surface using $KMnO_4$ / K_2CO_3 solutions

An aqueous potassium carbonate / potassium permanganate solution was prepared:

Solution IV: 4 g/liter K_2CO_3 with 0.05 g/liter $KMnO_4$.

The pH of the solution IV was determined to be 12. The potentiodynamic profile of a copper plate was measured in solutions IV. The results are depicted in Figure 12. From Figure 12 it is seen that the passivation potential of copper is 180 mV. It is seen that no pitting occurs during polarization.

MATERIALS, INSTRUMENTS AND EXPERIMENTAL METHODS

Materials:

All chemicals were obtained from Sigma-Aldrich Ltd. (St. Louis, Missouri, USA).

3.5mm diameter copper metal rods (99.9995 wt.%) were mounted in an epoxy resin to produce pencil-type copper electrodes. The electrodes were freshly wet-abraded to a 1200 grit finish prior to each experiment.

The morphology of etched copper surfaces was performed with rounded copper coupons (2 mm thick, 0.5 cm radius, 99.9995 wt.%) polished with 1 micron diamond paste.

Instruments:

Electrochemical measurements were performed in a three-electrode electrochemical cell with using a 273A EG&G Potentiostat. Working electrode

potentials were referenced to a saturated calomel electrode (SCE) connected through a Luggin-Habber capillary tip assembly. The counter electrode was a Pt-wire.

The morphology of the corroded copper surfaces was studied by scanning electron microscopy (SEM L30 Carl Zeiss Inc., Germany). Prior to observation,
5 specimens were washed in deionized water and air-dried.

It is appreciated that certain features of the invention, which are, for clarity, described in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features of the invention,
10 which are, for brevity, described in the context of a single embodiment, may also be provided separately or in any suitable subcombination.

Although the invention has been described in conjunction with specific embodiments thereof, it is evident that many alternatives, modifications and variations
15 will be apparent to those skilled in the art. Accordingly, it is intended to embrace all such alternatives, modifications and variations that fall within the spirit and broad scope of the appended claims. All publications, patents and patent applications mentioned in this specification are herein incorporated in their entirety by reference
20 into the specification, to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated herein by reference. In addition, citation or identification of any reference in this application shall not be construed as an admission that such reference is available as prior art to the present invention.

WHAT IS CLAIMED IS:

1. A composition useful for the formation of a passivating layer on a surface, the surface including more than about 5% copper by weight, comprising a solution having a pH equal to or greater than about 9 and having an oxidation potential sufficient to oxidize the surface to form copper oxides, wherein neither copper nor said copper oxides are substantially soluble in the composition.

2. The composition of claim 1, wherein the surface includes more than about 10% copper by weight.

3. The composition of claim 1, wherein the surface includes more than about 20% copper by weight.

4. The composition of claim 1, wherein the surface includes more than about 40% copper by weight.

5. The composition of claim 1, wherein the surface includes more than about 50% copper by weight.

6. The composition of claim 1, wherein the surface includes more than about 80% copper by weight.

7. The composition of claim 1, wherein said oxidation potential is more positive than about P_{pH} V relative to a saturated calomel reference electrode, where

$$P_{pH} = -0.05 \times pH + 0.425$$

pH being said pH of the composition.

8. The composition of claim 1, wherein said pH is between about 9 and about 10 and said oxidation potential is more positive than about -0.05V relative to a saturated calomel reference electrode.

9. The composition of claim 1, wherein said pH is between about 10 and about 11 and said oxidation potential is more positive than about -0.1V relative to a saturated calomel reference electrode.

10. The composition of claim 1, wherein said pH is between about 11 and about 12 and said oxidation potential is more positive than about -0.15V relative to a saturated calomel reference electrode.

11. The composition of claim 1, wherein said pH is between about 12 and about 13 and said oxidation potential is more positive than about -0.2V relative to a saturated calomel reference electrode.

12. The composition of claim 1, wherein said oxidation potential is more positive than a saturated calomel reference electrode by an oxidation potential selected from the group consisting of -0.2V, -0.15V, -0.10V, -0.05V, 0.0V, 0.05V, 0.10V, 0.15V, 0.20V, 0.25V, 0.3V, 0.35V, 0.40V, 0.45V, 0.50V, 0.55V, 0.60V, 0.65V and 0.7V.

12.5. The composition of claim 12, wherein said oxidation potential is more positive than a saturated calomel reference electrode by an oxidation potential of at least 0.0V.

13. The composition of claim 1, comprising

- a) a cation selected from the group of alkaline metal cations and alkaline earth metal cations; and
- b) an anion of a weak acid.

14. The composition of claim 13, wherein said cation is selected from the group consisting of Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} .

15. The composition of claim 13, wherein said weak acid has a pKa of greater than about 0.

16. The composition of claim 13, wherein said anion is selected from the group consisting of acetate, adipate, bicarbonate, bisulfate, carbonate, chloroacetate, citrate, crotonate, cyanate, glutarate, dihydrogen phosphate, hydrogen phosphate, hydrogen sulfate, hydroxide, d-lactate, l-lactate, d-malate, l-malate, maleate, d-mandelate, l-mandelate, malonate, oxalate, permanganate, phosphate, hydrogen phthalate, phthalate, propanoate, succinate, sulfanilate, sulfate, d-tartarate and l-tartarate.

17. The composition of claim 13, wherein said cation is K^+ and said anion is carbonate.

18. The composition of claim 13, wherein said cation is Cs^+ and said anion is carbonate.

19. The composition of claim 13, further comprising an oxidizing agent.

20. The composition of claim 19, wherein said oxidizing agent is selected from the group consisting of phenols, peroxides, permanganates, chromates, iodates, iron salts, aluminum salts, sodium salts, potassium salts, phosphonium salts, chlorates, perchlorates, persulfates and mixtures thereof.

21. The composition of claim 19, wherein said oxidizing agent is selected from the group consisting of phenol, KMnO_4 , KIO_3 , KBrO_3 , $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{K}_2\text{Cr}_2\text{O}_7$, V_2O_3 , H_2O_2 , HOCl , KOCl and KMgO_4 .

22. The composition of claim 19, wherein said oxidizing agent is KMnO_4 .

23. The composition of claim 1, substantially devoid of a film-forming agent.

24. The composition of claim 1, substantially devoid of a copper complexing agent.

25. The composition of claim 24, substantially devoid of ammonium cations.

26. The composition of claim 1, comprising abrasive particles.

27. The composition of claim 26, wherein said abrasive particles are metal oxides.

28. The composition of claim 27, wherein said metal oxide is selected from the group consisting of oxides of aluminum, cerium, germanium, silicon, titanium, zirconium and mixtures thereof.

29. The composition of claim 26, wherein said abrasive particles are chosen from the group comprising SiO_2 , CeO_2 , Al_2O_3 , SiC , Si_3N_4 and Fe_2O_3 .

30. The composition of claim 26, wherein said abrasive particles comprise between about 1% and 30% by weight of the composition.

31. A use of a composition of claim 1 for forming a passivating layer on a surface, said surface including more than about 5% copper by weight.

32. The composition of claim 31, wherein said surface includes more than about 10% copper by weight.

33. The composition of claim 31, wherein said surface includes more than about 20% copper by weight.

34. The composition of claim 31, wherein said surface includes more than about 40% copper by weight.

35. The composition of claim 31, wherein said surface includes more than about 50% copper by weight.

36. The composition of claim 31, wherein said surface includes more than about 80% copper by weight.

37. A method for the preparation of a composition useful for the formation of a passivating layer on a surface, the surface including more than about 5% copper by weight, comprising preparing a solution having a pH equal to or greater than about 9 and having an oxidation potential sufficient to oxidize the surface to form copper oxides, wherein neither copper nor said copper oxides are substantially soluble in the composition.

38. The method of claim 37, wherein said oxidation potential is more positive than a saturated calomel reference electrode by an oxidation potential selected from the group consisting of -0.2V, -0.15V, -0.10V, -0.05V, 0.0V, 0.05V, 0.10V, 0.15V, 0.20V, 0.25V, 0.3V, 0.35V, 0.40V, 0.45V, 0.50V, 0.55V, 0.60V, 0.65V and 0.7V.

38.5. The method of claim 38, wherein said oxidation potential is more positive than a saturated calomel reference electrode by an oxidation potential of at least 0.0V.

39. The method of claim 37, comprising

- a) providing a solution comprising water;
- b) adding to said solution a cation selected from the group consisting of alkaline metal cations and alkaline earth metal cations and an anion of a weak acid in an amount so that the pH of said solution is equal to or greater than about 9; and

c) adding to said solution an oxidizing agent so that the oxidation potential of said solution is more positive than about P_{pH} V relative to a saturated calomel reference electrode, where

$$P_{pH} = -0.05 \times pH + 0.425$$

pH being the pH of said solution.

40. The method of claim 39, wherein said oxidizing agent is selected from the group consisting of phenols, peroxides, permanganates, chromates, iodates, iron salts, aluminum salts, sodium salts, potassium salts, phosphonium salts, chlorates, perchlorates, persulfates and mixtures thereof.

41. The method of claim 37, further comprising adding abrasive particles to said solution.

42. The method of claim 41, wherein said abrasive particles are metal oxides.

43. The method of claim 42, wherein said metal oxide is selected from the group consisting of oxides of aluminum, cerium, germanium, silicon, titanium, zirconium and mixtures thereof.

44. The method of claim 41, wherein said abrasive particles are chosen from the group comprising SiO_2 , CeO_2 , Al_2O_3 , SiC, Si_3N_4 and Fe_2O_3 .

45. The method of claim 41, wherein said abrasive particles comprise between about 1% and 30% by weight of said solution.

46. A method of forming a passivating layer on a surface, the surface including more than about 5% copper by weight, comprising contacting the surface with a composition of claim 1.

47. A method for planarizing a surface, the surface including more than about 5% copper by weight, comprising abrading the surface in the presence of a composition of claim 1.

48. The method of claim 37, 46 or 47, wherein the surface includes more than about 10% copper by weight.

49. The method of claim 37, 46 or 47, wherein the surface includes more than about 20% copper by weight.

50. The method of claim 37, 46 or 47, wherein the surface includes more than about 40% copper by weight.

51. The method of claim 37, 46 or 47, wherein the surface includes more than about 50% copper by weight.

52. The method of claim 37, 46 or 47, wherein the surface includes more than about 80% copper by weight.

ABSTRACT

A composition that rapidly passivates copper-containing surface to yield a uniform layer of insoluble copper oxide, the composition being useful in chemical-mechanical planarization of copper-containing surfaces is disclosed. The composition is a solution having a pH of equal to or greater than 9 and having an oxidation potential sufficient to oxidize the surface to form non-soluble copper oxides. Also disclosed are methods of making and using the composition.

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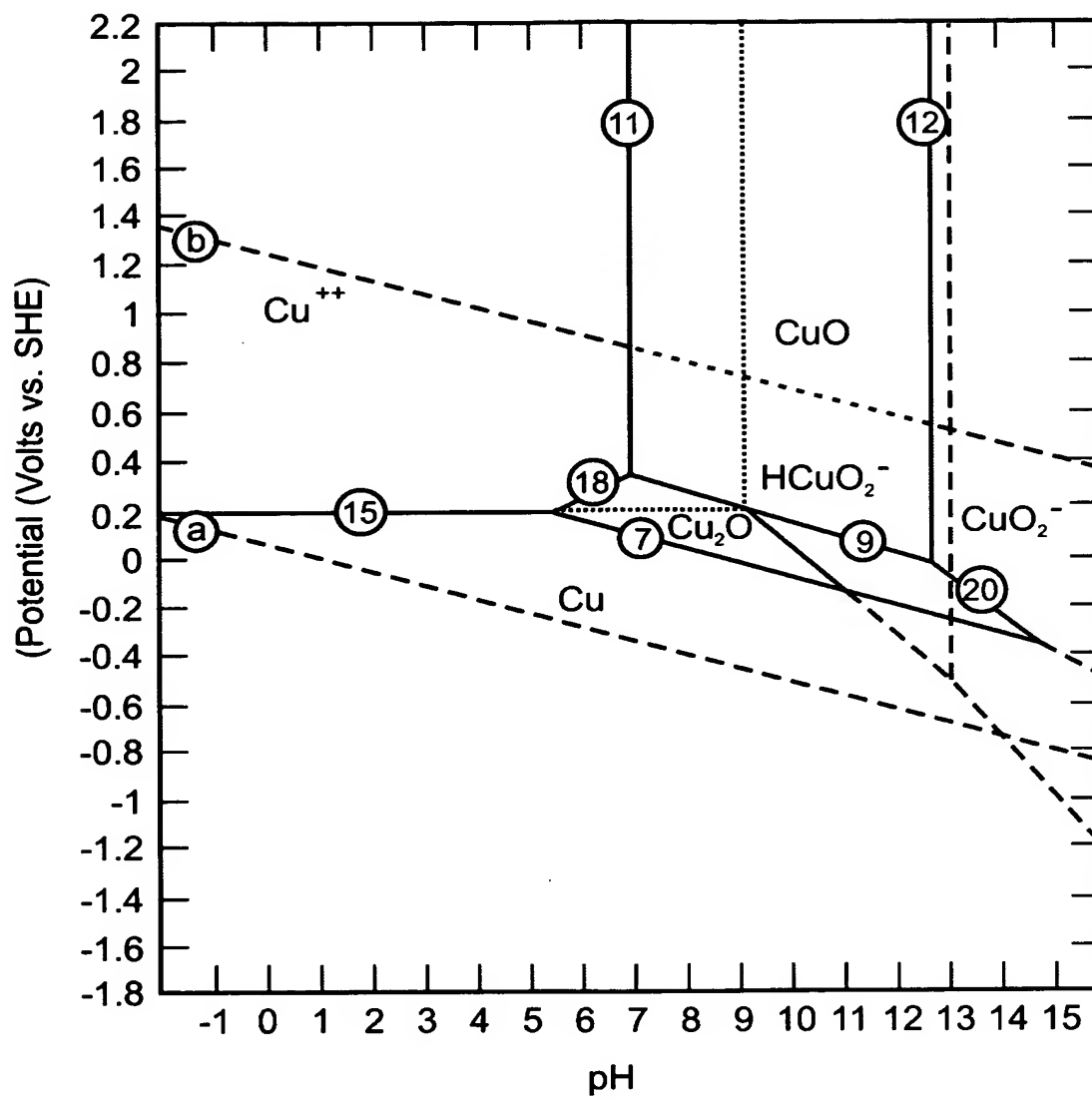


Fig. 1

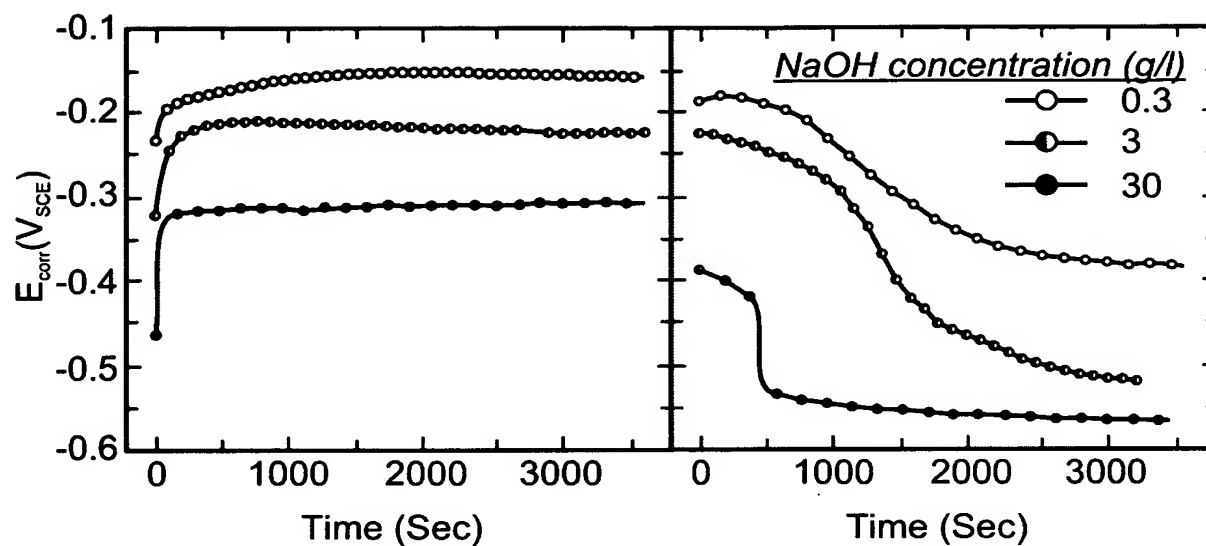


Fig. 2a

Fig. 2b

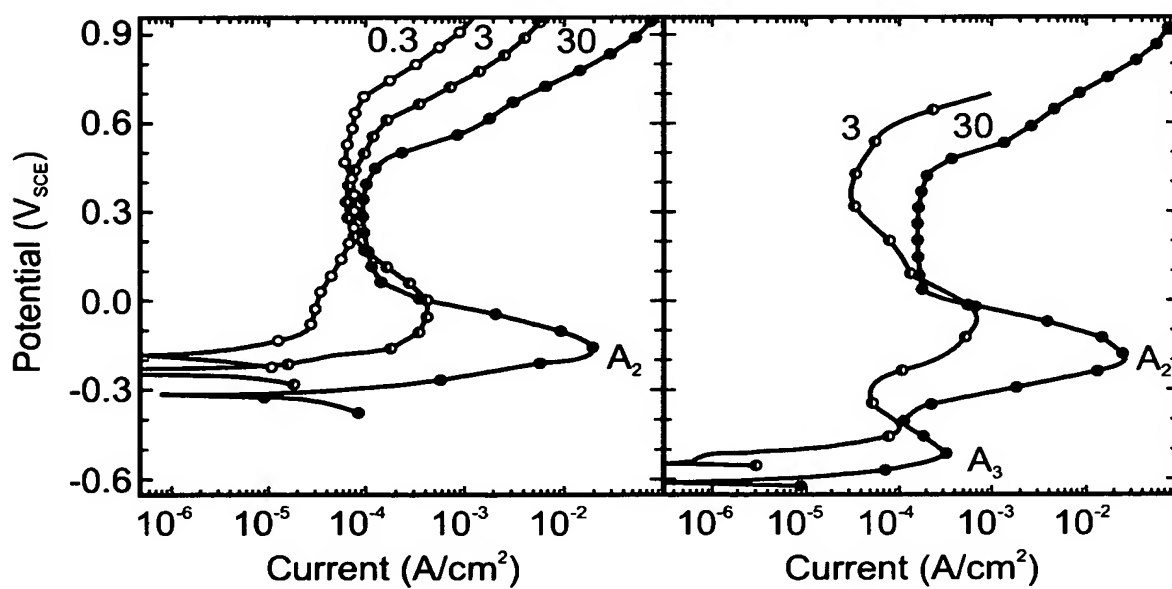


Fig. 3a

Fig. 3b

Fig. 4a

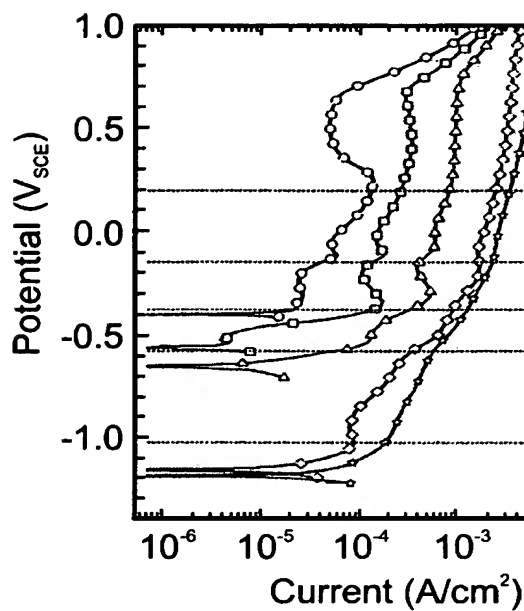
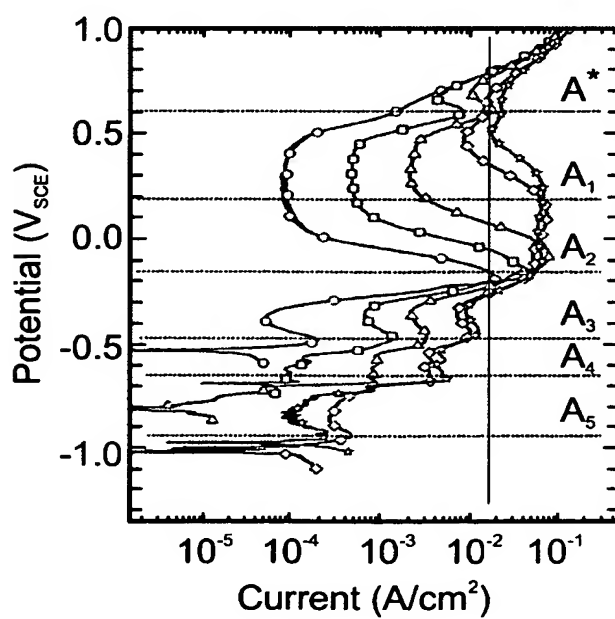
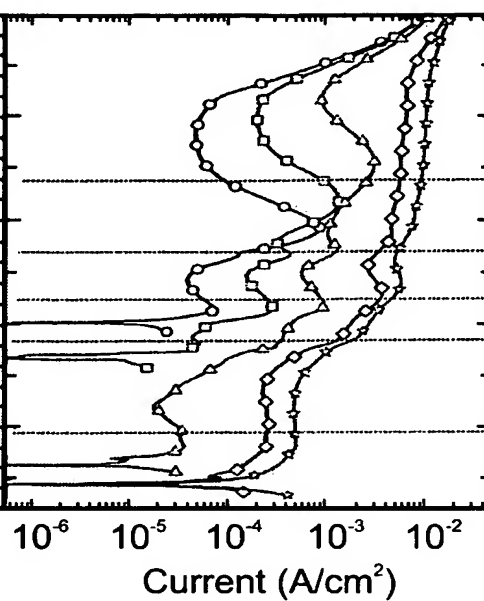


Fig. 4b



Scan rate ($m V/s$):

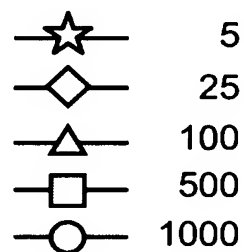


Fig. 4c

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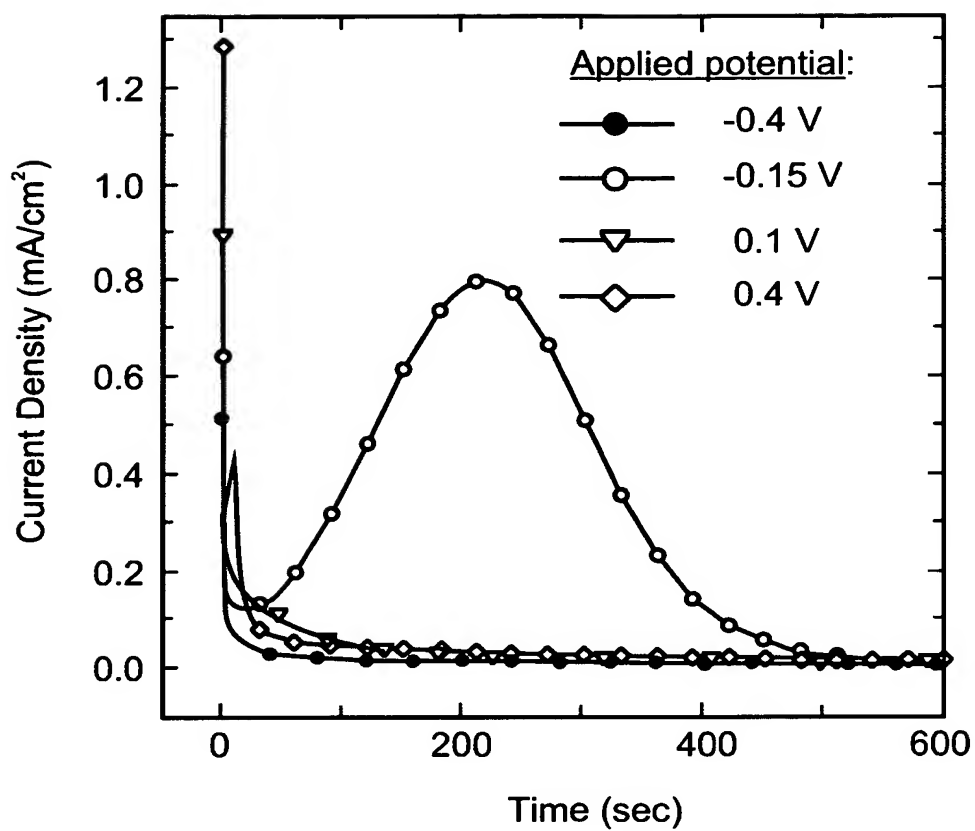


Fig. 5

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Polished surface

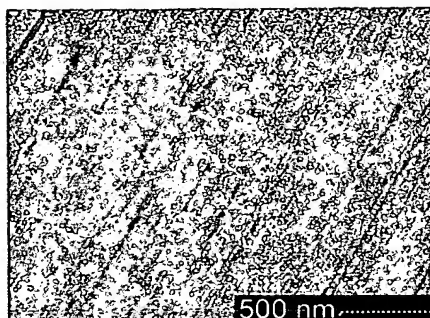


Fig. 6a

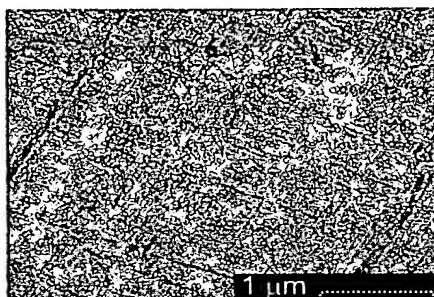
Peak A₃
-0.4 V

Fig. 6b

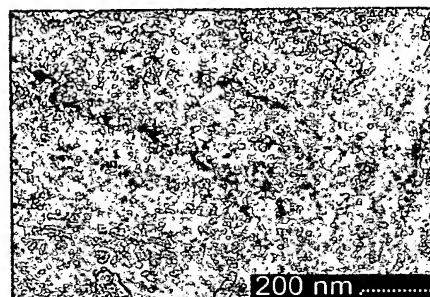


Fig. 6c

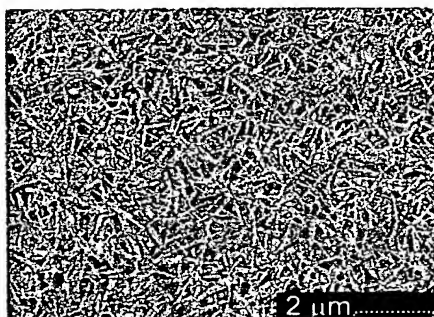


Fig. 6d

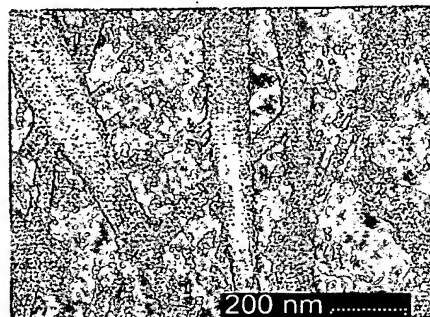


Fig. 6e

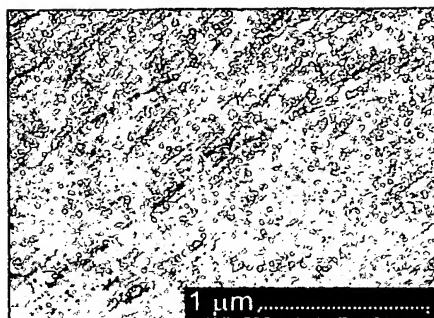
Peak A₁
0.3 V

Fig. 6f

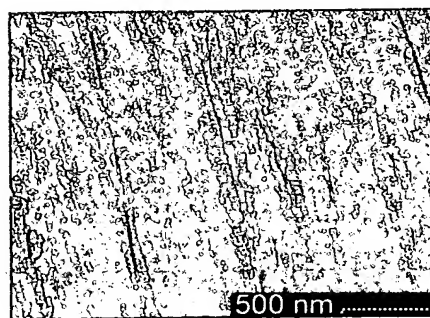


Fig. 6g

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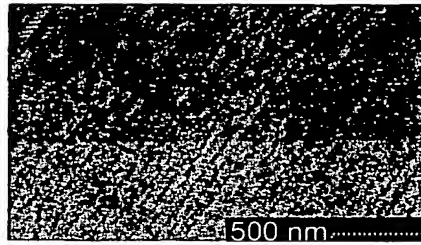


Fig. 7a

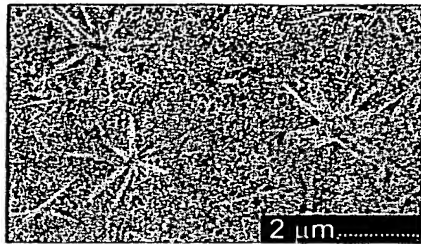


Fig. 7b

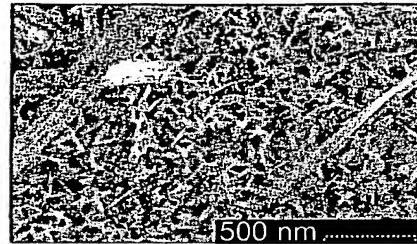


Fig. 7c

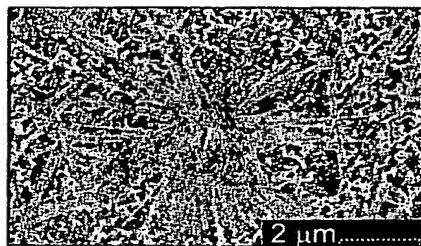


Fig. 7d

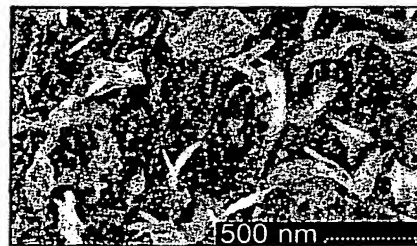


Fig. 7e

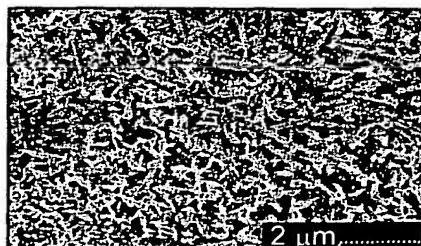


Fig. 7f

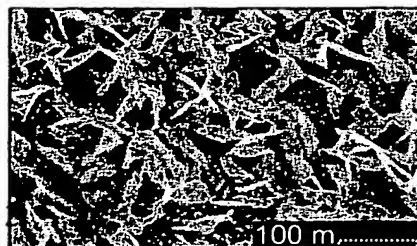


Fig. 7g

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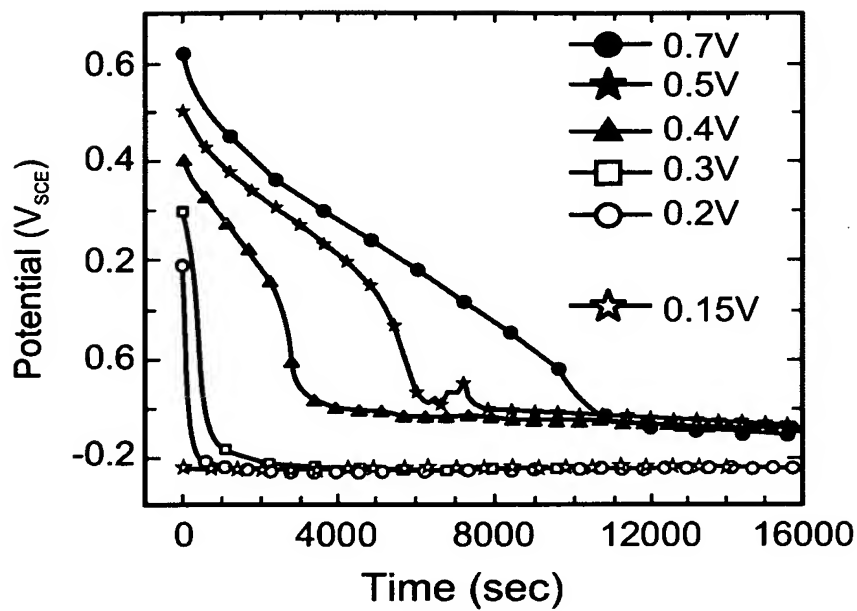


Fig. 8

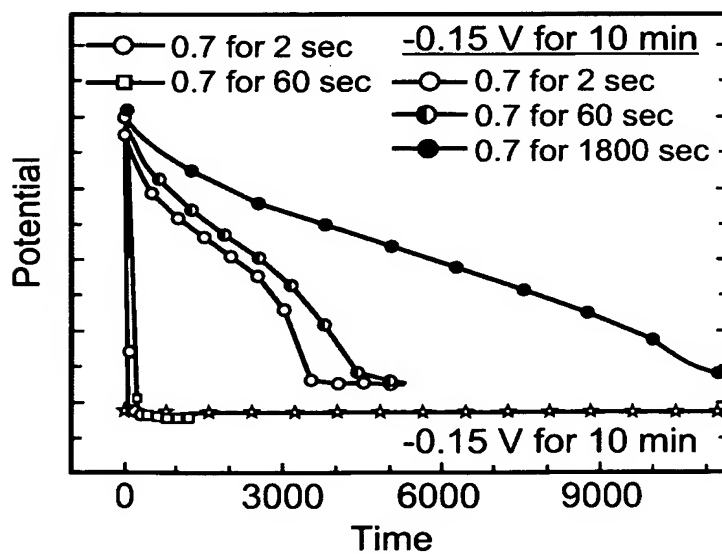


Fig. 9

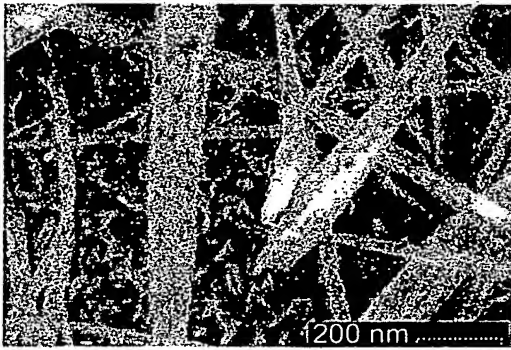


Fig. 10a

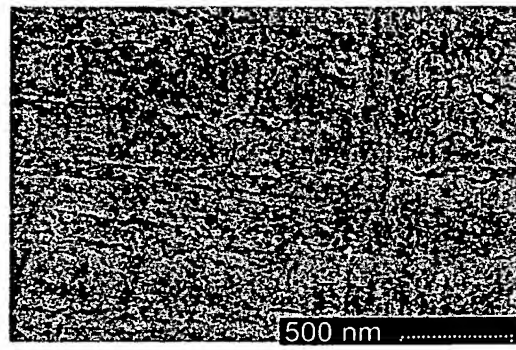


Fig. 10b

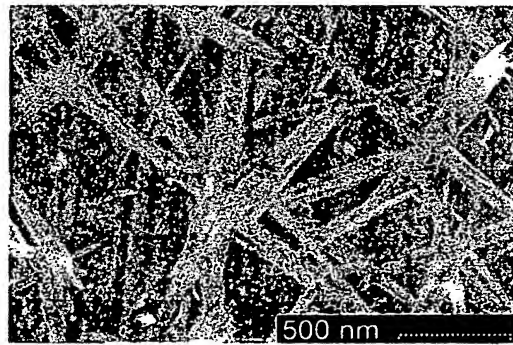


Fig. 10c

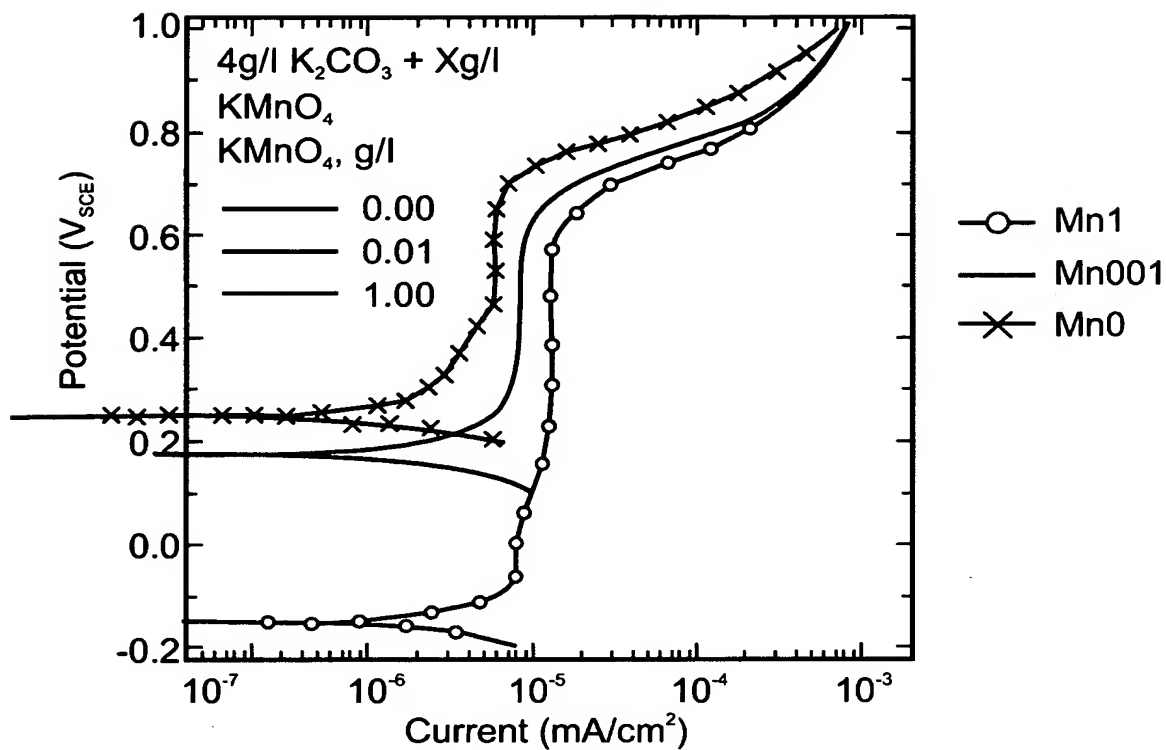


Fig. 11

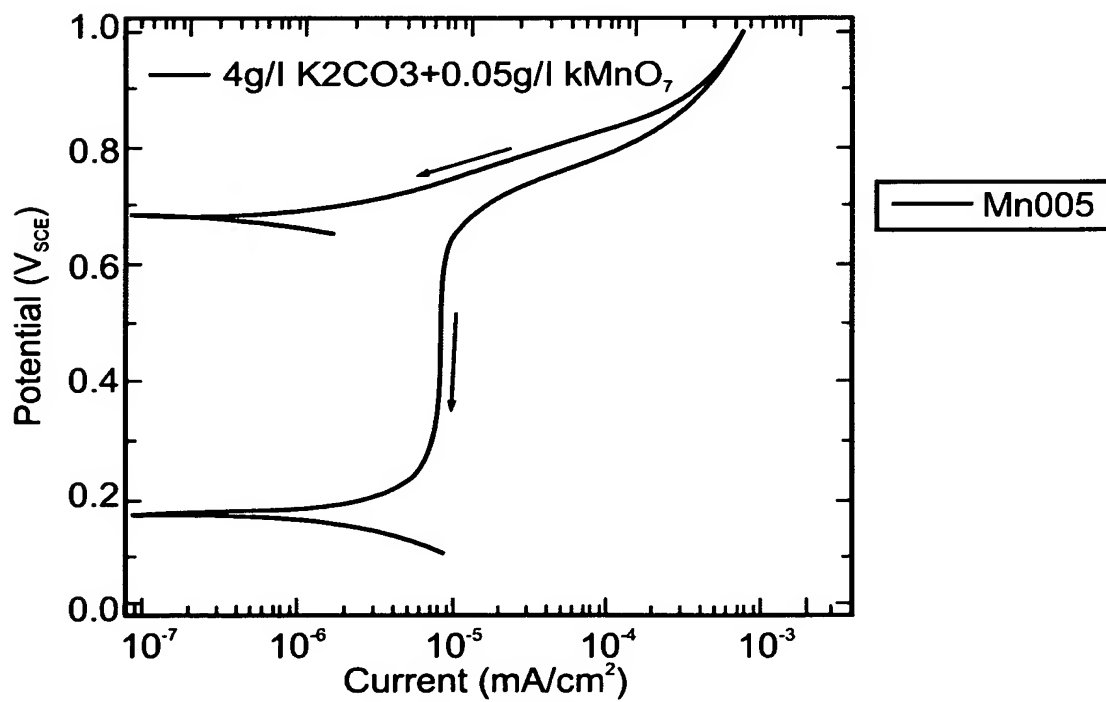


Fig. 12